



# Fast-regenerable sulfur dioxide absorbents for lean-burn diesel engine emission control

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## ABSTRACT

It is known that sulfur oxides contribute significantly and deleteriously to the overall performance of lean-burn diesel engine after-treatment systems, especially in the case of NO<sub>x</sub> traps. A silica-supported silver-based, fast regenerable SO<sub>2</sub> absorbent has been developed and will be described. Over a temperature range of 300–550 °C, it absorbs SO<sub>2</sub> present in a simulated exhaust gas during the lean cycles, and can be fully regenerated by short rich gas cycles at the same temperature. The preferred silica support is fumed silica. The thermal instability of Ag<sub>2</sub>O under fuel-lean conditions at 230 °C and above makes it possible to rapidly regenerate the sulfur-loaded absorbent during the fuel-rich cycle due to the lack of a requirement to simultaneously reduce Ag<sub>2</sub>O to Ag. Ag particles can also effectively oxidize SO<sub>2</sub> to SO<sub>3</sub>, facilitating the formation of Ag<sub>2</sub>SO<sub>4</sub> and requiring no additional oxidation catalysts. This absorbent shows great potential to work under the same lean-rich cycling conditions as those imposed on the NO<sub>x</sub> traps, and thus can protect the downstream particulate filter and the NO<sub>x</sub> trap from sulfur poisoning.

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## 1. Introduction

Lean-burn diesel engines have many advantages over gasoline spark-ignited engines, including better fuel efficiency and lower CO<sub>2</sub> emissions. However, the emissions of particulates and NO<sub>x</sub> from diesel engines pose an important environmental problem. A major effort to reduce these emissions is to implement particulate filters and NO<sub>x</sub> conversion devices [1]. One promising approach, based on NO<sub>x</sub> trap technology [2], stores NO<sub>x</sub> as an alkali or alkaline earth nitrate during normal operation (fuel-lean conditions) and releases nitrogen as N<sub>2</sub> during a brief fuel-rich reduction step (rich conditions). Sulfur oxides contribute significantly and deleteriously to the overall performance of the NO<sub>x</sub> trap system. During the lean conditions, SO<sub>2</sub> is oxidized to SO<sub>3</sub> by the precious metals in the NO<sub>x</sub> trap, which reacts with alkali or alkaline earth oxides also present in the NO<sub>x</sub> trap to form sulfates. These sulfates cannot be removed easily during the subsequent rich cycles, which leads to the need for a high-temperature desulfurization (“desulfation”) step [2–4]. These desulfation treatments result in a gradual degradation of the NO<sub>x</sub> trap over the course of many cycles. To remove unburned hydrocarbons, an oxidation catalyst such as Pt/Al<sub>2</sub>O<sub>3</sub> is needed. SO<sub>2</sub> in the exhaust is also oxidized to SO<sub>3</sub> by this oxidation catalyst, which leads to the formation of liquid particulates

containing sulfuric acid in the exhaust. SO<sub>3</sub> also reacts with the Al<sub>2</sub>O<sub>3</sub> oxidation catalyst support to form Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, which further degrades the performance. Although low sulfur diesel fuels are being used since 2006 [5], the ~15 ppmw sulfur level in these fuels is still too high for the emission after-treatment systems, and the need for improved sulfur oxide management remains.

To protect the entire after-treatment system, one possible approach is to include a separate sulfur trap upstream of the particulate filter and the NO<sub>x</sub> trap. Dedicated, high capacity sulfur absorbents were developed previously in our group [6–8]. Their SO<sub>2</sub> capacity can be as high as 70 wt%. However, as a dedicated sulfur trap, it needs to be replaced regularly for off-line regeneration. We therefore targeted development of an on-line regenerable sulfur trap, which can oxidize and absorb SO<sub>2</sub> (SO<sub>3</sub>) during the lean conditions and release the absorbed sulfur during the short rich conditions used for the NO<sub>x</sub> trap regeneration. Ideally, under rich conditions, sulfur in the SO<sub>x</sub> trap is released as SO<sub>2</sub>, which does not react strongly with the downstream particulate filter and the NO<sub>x</sub> trap materials [9–11].

Cu-doped Al<sub>2</sub>O<sub>3</sub> has been widely studied as a regenerable flue gas sulfur oxide absorbent [12–16]. It reacts with SO<sub>2</sub> and O<sub>2</sub> at ~350 °C to form CuSO<sub>4</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. The sulfated absorbent can be regenerated by reduction in H<sub>2</sub> or CH<sub>4</sub> at 400–500 °C, followed by oxidation in air at 500 °C to re-form the copper oxide and alumina phases. The required reaction conditions in this absorption/regeneration process make it extremely challenging to use Cu-doped Al<sub>2</sub>O<sub>3</sub> as an on-line regenerable sulfur trap [17–19]. Even

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**Table 1**Composition of simulated diesel engine exhausts used in the study<sup>a</sup>.

Exhaust	CO	CO <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	H <sub>2</sub>	SO <sub>2</sub>	O <sub>2</sub>	NO <sub>2</sub>	NO	N <sub>2</sub>
Lean	–	5%	–	–	5.15 ppm	12%	20 ppm	180 ppm	Balance
Rich	2%	12.5%	333 ppm	2%	–	–	–	–	Balance

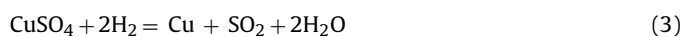
<sup>a</sup> For some tests, feed gases with steam or with a higher SO<sub>2</sub> concentration (25 ppm) were used, which is specified in the text.

if inert supports are used, the copper oxide/copper metal redox reactions which are taking place in parallel with the SO<sub>x</sub> absorption (i.e. fuel-lean oxidation step) and desorption (i.e. fuel-rich reduction step) make it very difficult to develop Cu-based fast regenerable SO<sub>x</sub> traps. Reactions (1)–(4) give the key reactions for Cu-based SO<sub>x</sub> traps with inert supports, using H<sub>2</sub> as a representative reductant. Under fuel-rich cycles, the un-sulfated CuO will react with reducing gases to form metallic Cu, which not only causes a fuel penalty, but also prevents the system from fast regeneration.

Under normal fuel-lean operation conditions:



Under fuel rich NO<sub>x</sub> trap regeneration conditions:



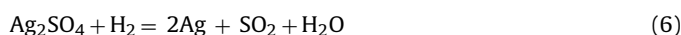
A regenerable SO<sub>x</sub> absorber based on AgO/Al<sub>2</sub>O<sub>3</sub> was proposed by Nakatsuji et al., which showed good SO<sub>2</sub> absorption during lean conditions and the potential for fast regeneration during short rich cycles at temperatures greater than 350 °C [10]. However, the long-term durability of this system is poor [20], quite possibly due to the formation of stable aluminum sulfate Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and silver aluminate AgAlO<sub>2</sub> [21,22]. Kylhammar et al. reported a regenerable CeO<sub>2</sub>-based SO<sub>x</sub> trap, which can absorb SO<sub>2</sub> at 250 °C and can be regenerated at above 600 °C [23]. Similar results were also reported by Le Phuc, et al. with a Pt/Ce<sub>x</sub>Zr<sub>1-x</sub>O<sub>2</sub> system [24]. Since a thermal swing process was used for sulfur release in both cases, a fast regeneration is impossible.

In this study, we report a fast regenerable Ag–SiO<sub>2</sub> SO<sub>x</sub> absorbent which can work under the same lean-rich cycling conditions as imposed on the NO<sub>x</sub> traps. The justification for the choice of silver is the thermal instability of Ag<sub>2</sub>O under lean conditions. Ag<sub>2</sub>O decomposes to metallic Ag and O<sub>2</sub> at  $T \geq 230$  °C in air. This means that if operating above this temperature, no reductant is consumed through a parallel reduction of un-used Ag<sub>2</sub>O during the rich cycle regeneration of Ag<sub>2</sub>SO<sub>4</sub>, and therefore fast regeneration is possible even at high silver loadings. Reactions (5) and (6) give SO<sub>2</sub> absorption and desorption reactions during lean and rich cycles, using H<sub>2</sub> as a representative reductant in rich exhausts. Fumed silica was selected as the preferred supporting material for small Ag particles. Unlike the Al<sub>2</sub>O<sub>3</sub> supports, fumed SiO<sub>2</sub> is chemically inert under the NO<sub>x</sub> trap operating conditions. The effect of Pt co-doping was studied in this work. Pt was added as a catalyst to oxidize SO<sub>2</sub> to SO<sub>3</sub> for better sulfur absorption. However, it turned out that Pt addition was unnecessary.

Under normal fuel-lean operation condition:



Under fuel rich NO<sub>x</sub> trap regeneration condition:



## 2. Experimental

Except otherwise specified, all the chemicals were purchased from Aldrich. The absorbents were prepared typically by incip-

ient wetness impregnation, using aqueous solution mixtures of Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> and AgNO<sub>3</sub> onto a high surface area support, followed by drying and calcining at 500 °C in air. Absorbents with different Pt and Ag loadings were prepared. For most studies, Cab-O-Sil® amorphous fumed silica with surface area ~200 m<sup>2</sup>/g (Cabot Corporation, Tuscola, IL, USA) was employed as the absorbent support. Other supports, such as silica gel, mesoporous silica MCM41 (surface area: ~900 m<sup>2</sup>/g), γ-Al<sub>2</sub>O<sub>3</sub> (from Engelhard Corporation, surface area: ~150 m<sup>2</sup>/g), P25 TiO<sub>2</sub> (Degussa Corporation, surface area: ~60 m<sup>2</sup>/g), ZrO<sub>2</sub> (Daiichi Kigenso Kagaku Kogyo Co. Ltd. Japan, surface area: ~96 m<sup>2</sup>/g) were also evaluated. The absorbents were tested as 40–80 mesh or 80–200 mesh granules, formed by pressing finely ground powders into a tablet at 20,000 psi for 5 min followed by crushing and screening. Typical performance measurements employed a 50 mg absorbent sample.

Sulfation and desulfation tests and lean-rich cycling tests were carried out using an AMI-200R-HP unit (Altamira Instruments, Pittsburg, PA, USA), which automatically switched the feed to the heated reactor between lean and rich exhaust gas compositions at given time intervals. The compositions of the lean and rich exhaust simulants are given in Table 1. The gas compositions downstream of the absorbent were measured using a mass spectrometer (MS, Dymaxion, Ametek Inc., Pittsburg, PA, USA). The sulfur concentrations were measured using a Hewlett-Packard 6890 gas chromatograph (GC) equipped with a Sulfur Chemiluminescent Detector (SCD), which was described previously in detail [25]. During the experimental run, the GC-SCD analytical system was operated continuously, sampling the effluent once per minute. The minimum detection limit of the system to sulfur was approximately 50 ppb.

Powder XRD measurements and analyses were conducted with a Philips PW3050 diffractometer using Cu Kα radiation and JADE, a commercial software package. Sample powders were mounted in a front-loading, shallow-cavity zero-background quartz holder, and the data were collected from 5° to 75° 2θ in step-scan mode using steps of 0.02°. Transmission electron microscopy (TEM) analysis was carried out on a JEOL JEM 2010F microscope. Selected area Energy Dispersive X-ray Spectroscopy (EDS) was performed on regions of interest using a Links EDS system equipped on the microscope. To obtain TEM images, the as-synthesized powder was dispersed in acetone solution, and then deposited on a Cu-carbon grid.

## 3. Results and discussion

### 3.1. Sulfation and desulfation behavior of 1 wt% Pt and 5 wt% Ag-doped fumed SiO<sub>2</sub>

Fig. 1 shows sulfation/desulfation test results for sample 86D (1 wt% Pt–5 wt% Ag-fumed SiO<sub>2</sub>). The purpose of this test was to determine the SO<sub>2</sub> absorption performance under lean conditions and the SO<sub>2</sub> desorption performance under rich conditions. The test was carried out as follows: first, the absorbent was heated from room temperature to 560 °C at 10 °C/min in the simulated lean feed gas at 100,000 h<sup>–1</sup> gas hourly space velocity (GHSV), during which SO<sub>2</sub> absorption occurred (sulfation test). After cooling down in air at 50,000 h<sup>–1</sup> GHSV to 50 °C, the sample was heated to 560 °C at 10 °C/min in the simulated rich feed at 20,000 h<sup>–1</sup> GHSV,

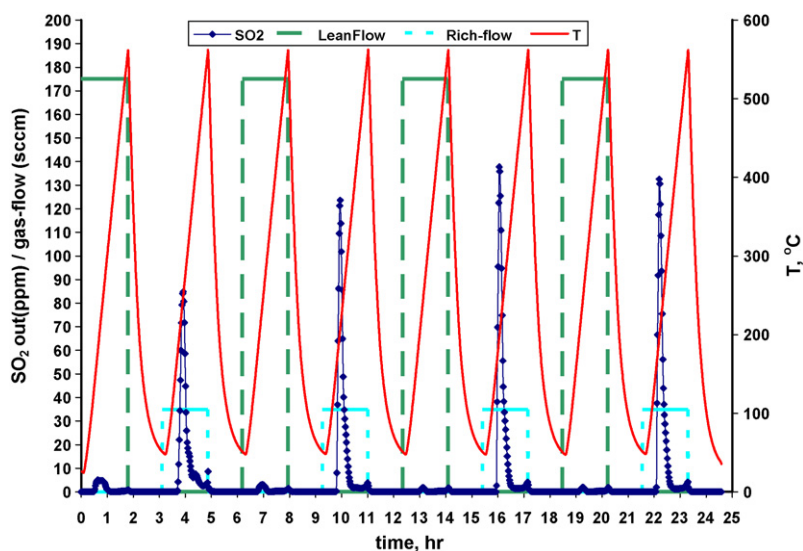


Fig. 1. Sulfation/desulfation tests of sample 86D (1 wt% Pt–5 wt% Ag–SiO<sub>2</sub>).

during which SO<sub>2</sub> desorption occurred (desulfation test). After cooling down again to 50 °C in air, the sample was heated to 560 °C in the lean feed for a second sulfation test, and then a second desulfation followed after first cooling down to 50 °C. During the test, the SO<sub>2</sub> concentration in the off-gas was measured continuously using the GC-SCD system. Fig. 1 shows the overall result of four such sulfation/desulfation cycles.

From each sulfation test, SO<sub>2</sub> breakthrough (defined at 200 ppb SO<sub>2</sub> in the off-gas) capacities at three different temperatures were obtained. This is shown in detail in Fig. 2. The initial low temperature capacity at T1 was calculated (~200 °C) based on the SO<sub>2</sub> concentration profile in the feed and the related time-on-stream. Above T1, the SO<sub>2</sub> concentration in the exit stream exceeded 200 ppb. However, as the temperature ramped upward, the SO<sub>2</sub> concentration continued to increase and then decreased, until SO<sub>2</sub> in the effluent was again at 200 ppb (at T2). The capacity at T2 was again calculated based on the time-on-stream and the SO<sub>2</sub> concentration profile in the off gas. Eventually at T3, the SO<sub>2</sub> in the effluent once again reached 200 ppb and the capacity at that temperature was again calculated. Ag<sub>2</sub>SO<sub>4</sub> was formed after this sample experienced extended sulfation treatment at 550 °C with high con-

centration SO<sub>2</sub>, which confirmed our previous assumption that the sulfation of this absorbent during lean cycles is through Reaction (5).

From each desulfation test, a temperature-programmed reduction curve was obtained. Figs. 3 and 4 summarize the SO<sub>2</sub> absorption and desorption information from the four sulfation–desulfation cycles. The SO<sub>2</sub> absorption (sulfation) capacity as a function of temperature, shown in Fig. 3, appeared to have linear behavior, allowing estimation of total capacity at any operating temperature over a broad temperature range from about 200 to 450 °C. After the first cycle, this absorbent showed good and reproducible SO<sub>2</sub> absorption behavior. The results in Fig. 4 show that once steady state operation of the absorbent had been achieved (starting at the second cycle), full desulfation could be achieved at approximately 300 °C and higher. Based on the sulfur balance, more than 90% of sulfur that was absorbed during the stable sulfation steps was removed during the subsequent desulfation steps below 300 °C. This is consistent with a constant sulfation performance of the absorbent after the first cycle, as shown in Fig. 3.

Due to the existence of sub-surface oxygen within the fresh Ag particles (the fresh absorbent was calcined at 500 °C in air) [26], more SO<sub>2</sub> was absorbed during the first sulfation step than other sulfation steps. As a result, a higher temperature was needed during the first desulfation step. Full regeneration is not only determined

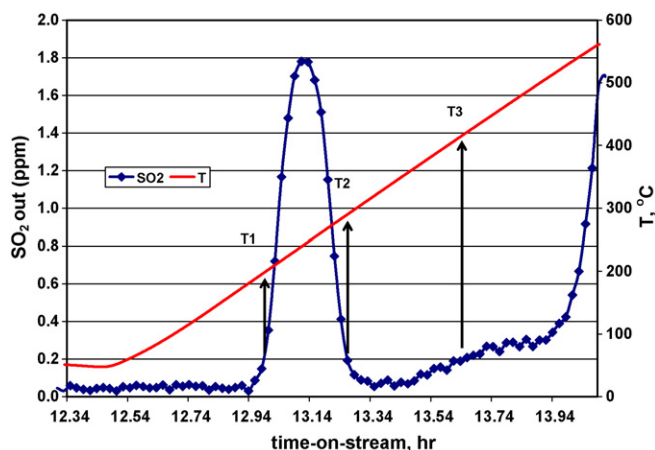


Fig. 2. A typical sulfation step from the sulfation/desulfation tests with sample 86D. SO<sub>2</sub> 200 ppb breakthrough capacities at three different temperatures, T1, T2, and T3, can be calculated from time-on-stream and the SO<sub>2</sub> concentration profile in the off-gas.

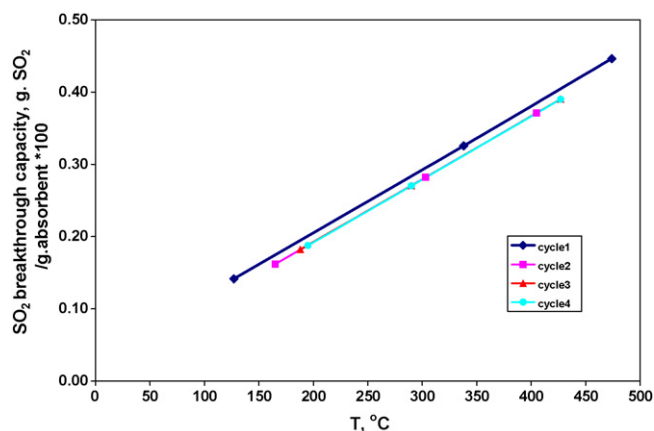


Fig. 3. SO<sub>2</sub> breakthrough capacity at different temperatures for sample 86D during successive sulfation cycles.

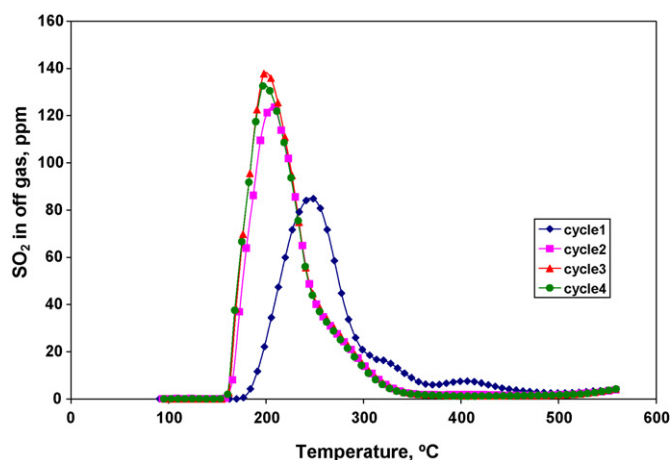


Fig. 4. Temperature effect on  $\text{SO}_2$  desorption of sulfated sample 86D during successive desulfation cycles.

by the rich feed composition and the regeneration temperature, but also by the sulfation level of the absorbent. The more sulfur it absorbs, the more difficult it is to regenerate. The frequent lean-rich cycling protocol for the  $\text{NO}_x$  trap should be able to prevent deep sulfation of the Ag particles during lean cycles and facilitate fast regeneration of the surface  $\text{Ag}_2\text{SO}_4$  at a temperature as low as  $300^\circ\text{C}$  during the rich cycles.

### 3.2. 1 wt% Pt and 5 wt% Ag-doped fumed $\text{SiO}_2$ as a fast-regenerable sulfur dioxide absorbent

A fast regenerable  $\text{SO}_x$  absorbent must be able to absorb  $\text{SO}_x$  over a wide temperature range, and upon changing the gas feed to a rich composition, the sulfated absorbent must be rapidly regenerated at the same temperature. To verify that the Pt–Ag– $\text{SiO}_2$  system is a good candidate for fast regenerable  $\text{SO}_2$  traps, sample 86D was evaluated over a wide range of lean-rich cycling conditions at a temperature range of  $200$ – $550^\circ\text{C}$ . Fig. 5 shows a typical off-gas composition measured by the mass spectrometer as sample 86D was cycling with 20 s rich feed at  $10,000\text{ h}^{-1}$  GHSV and 4 min lean

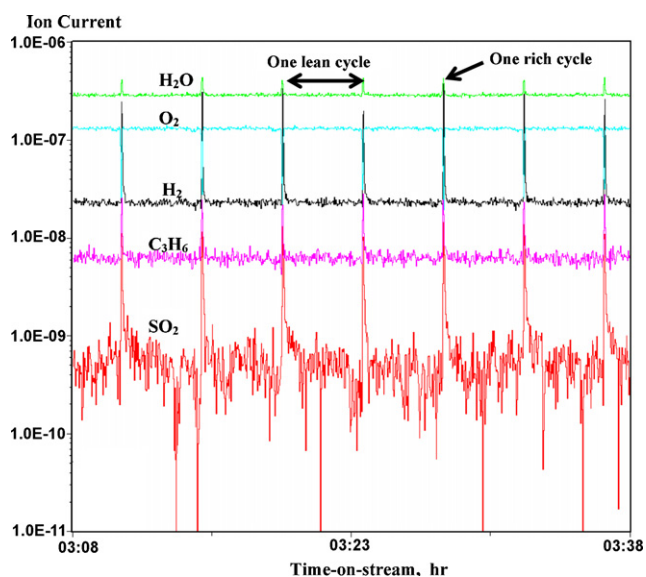


Fig. 5. A typical off-gas composition measured by a mass spectrometer at  $300^\circ\text{C}$  during a lean-rich cycling test with sample 86D. Test condition: cycling with 20 s rich feed at  $10,000\text{ h}^{-1}$  GHSV and 4 min lean feed at  $50,000\text{ h}^{-1}$  GHSV. Each peak corresponds to one rich cycle.

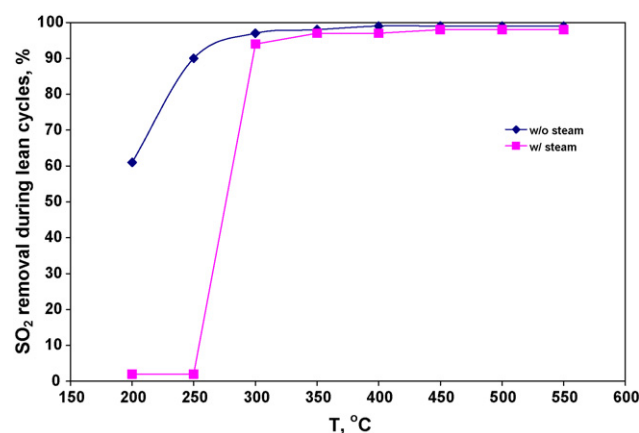
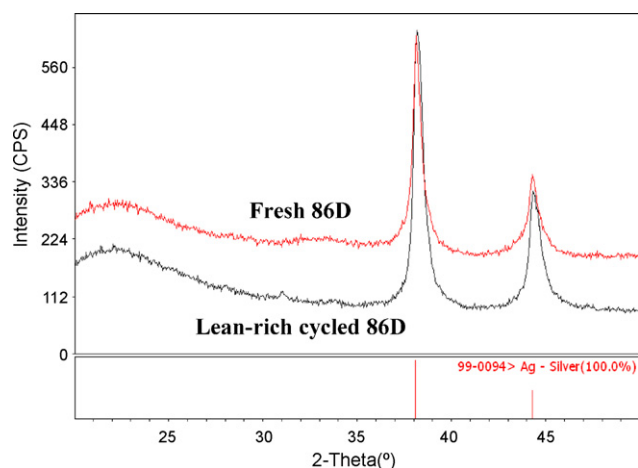


Fig. 6.  $\text{SO}_2$  removal efficiency of sample 86D (1 wt% Pt–5 wt% Ag– $\text{SiO}_2$ ) during lean cycles at different temperatures. Test condition: cycling with 20 s rich feed at  $10,000\text{ h}^{-1}$  GHSV and 4 min lean feed with 5.15 ppm  $\text{SO}_2$  at  $100,000\text{ h}^{-1}$  GHSV. See Table 1 for the dry feed composition. For the test with steam, the lean feed had 1.2% steam and the rich feed had 12% steam.

feed at  $50,000\text{ h}^{-1}$  GHSV at  $300^\circ\text{C}$ . During the lean cycles, more than 97% of the  $\text{SO}_2$  present in the exhaust stream was absorbed as measured by GC. During the short rich cycle period, a large amount of  $\text{SO}_2$  was released. No  $\text{SO}_2$  absorption/desorption was observed with absorbent-free blank system. Inert gases, such as Ar or  $\text{N}_2$ , could also partially regenerate the sulfated absorbent, but not as efficiently as rich cycle exhausts. Our system could not accurately quantify the  $\text{SO}_2$  concentration released during rich cycles since each GC measurement took about 1 min and each rich cycle only lasted 20 s. However, based on the combined information from the GC and the MS, the maximum  $\text{SO}_2$  concentration eluted during the rich cycles was as high as 100 ppm. No noticeable carbonyl sulfide (COS) or other sulfur-containing species were released during the rich cycles, based on the MS measurements, indicating that virtually all the sulfur was desorbed as  $\text{SO}_2$ .  $\text{SO}_2$  is a preferred sulfur product during rich cycles, not only because it does not react strongly with the downstream particulate filters and  $\text{NO}_x$  traps, it also does not pose an odor problem as does  $\text{H}_2\text{S}$  or a toxicity problem, as does COS. This cycling test was repeated for a total duration of 18.5 h (256 lean/rich cycles). During the entire test, the absorbent showed very stable performance, i.e. repeatable  $>97\%$   $\text{SO}_2$  removal during the lean cycles. This indicates that the absorbent was effectively regenerated during the rich cycles. Without regeneration, according to Fig. 3, the same amount of material would only last about 1 h under the tested condition before the 200 ppb  $\text{SO}_2$  breakthrough would occur. Fig. 6 gives the performance of this absorbent when cycling with 20 s rich feed at  $10,000\text{ h}^{-1}$  GHSV and 4 min lean feed at  $100,000\text{ h}^{-1}$  GHSV. Both dry and wet exhaust gas simulants were used. At low temperature range ( $<300^\circ\text{C}$ ), water hampered the performance of this absorbent, possibly because water molecules covered up part of absorbent's surface. Also, according to Eq. (6), water is produced during the rich cycle desorption of sulfur dioxide. The existence of 12% steam in the rich exhaust thus prevented the sulfur-loaded absorbent from complete regeneration at low temperatures. Nevertheless, even when wet exhaust simulants were used, this absorbent still showed stable  $>94\%$  sulfur removal at  $300^\circ\text{C}$ , and  $>97\%$  sulfur removal at  $350$ – $550^\circ\text{C}$ . Sample 86D was also evaluated under milder conditions (i.e. longer rich cycles and shorter lean cycles with slower flow rates). Slightly better sulfur removal performance was observed under these conditions.

Fresh and lean-rich cycled sample 86D (cycled for 32 h over a temperature range of  $200$ – $550^\circ\text{C}$ ) were analyzed using XRD, and TEM-EDS. Figs. 7 and 8 show their XRD patterns and TEM images





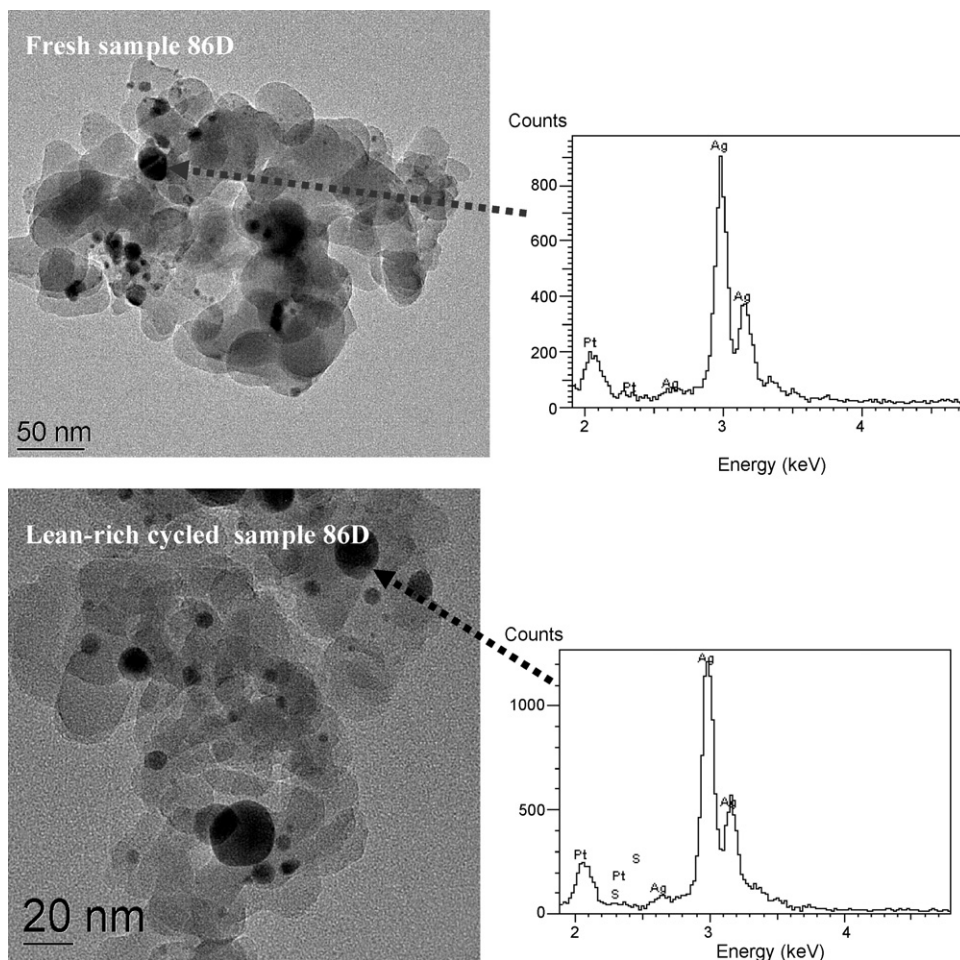
**Fig. 7.** XRD patterns of fresh and lean-rich cycled sample 86D (1 wt% Pt–5 wt% Ag–SO<sub>2</sub>).

along with EDS spectra. Well-mixed small Ag–Pt alloy particles were formed on the fumed silica support in the fresh sample. A slight metal sintering effect was observed after lean-rich cycling as the Ag/Pt alloy particles become more spherical. A modest particle size increase was observed based on XRD line broadening and TEM analysis. Also, EDS spectra showed there was no detectable sulfur in the lean-rich cycled samples, indicating that most of the sulfur was desorbed during the short rich cycles.

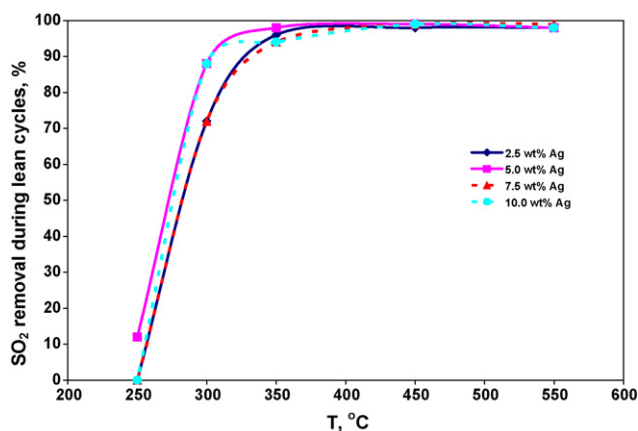
Sintering is always a problem for small Ag particles. Yang et al. [27] reported that under reducing conditions, silver clusters of 100–750 nm are stable up to 700 °C. However, under oxidizing conditions, the silver cluster surface is oxidized and roughened below 300 °C, and agglomeration and migration occurs above 350–400 °C. For this reason, industrial application of Ag oxidation catalysts is always carried out at a temperature lower than 300 °C [26]. However, Fig. 8 shows that the nano-sized Ag particles on the SiO<sub>2</sub> surface were fairly stable under lean-rich cycling conditions. After treatment for 32 h at a temperature range of 200–550 °C, a large fraction of the Ag particles below 10 nm were still stable. The enhanced stability of Ag particles possibly came from the lean-rich cycling protocol.

### 3.3. Optimization of the absorbent's formulation

To optimize the absorbent performance, absorbents with different Ag and Pt loading were synthesized. These absorbents were screened under lean-rich cycling, with 20 s rich feed at 20,000 h<sup>−1</sup> GHSV and 4 min lean feed at 50,000 h<sup>−1</sup> GHSV. Lean feeds with high sulfur concentration (25 ppm SO<sub>2</sub>) were used to accelerate the screening tests. Figs. 9 and 10 give the results. Minimal effects of Ag and Pt loadings on the absorbent's performance were observed. Although lean feed gas with high concentration SO<sub>2</sub> (25 ppm) was used in these tests, with ≥2.5 wt% Ag loading (the molar ratio of Ag to total sulfur fed in >20), all absorbents would have enough capacity for complete sulfur removal during each lean cycle. As a result, no Ag loading effect on the absorbent's performance was



**Fig. 8.** TEM images with EDS spectra of fresh (top) and lean-rich cycled (bottom) sample 86D (1 wt% Pt–5 wt% Ag–SO<sub>2</sub>).

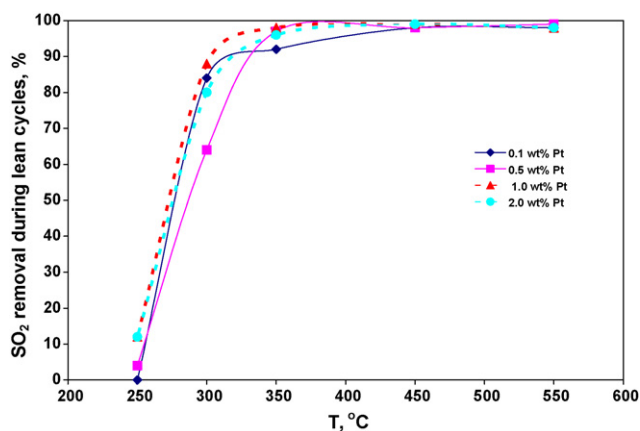


**Fig. 9.** Ag loading effect on the performance of 1 wt% Pt-*x* wt% Ag-SiO<sub>2</sub> absorbents. Cycling with 20 s rich feed at 20,000 h<sup>-1</sup> GHSV and 4 min lean feed with 25 ppm SO<sub>2</sub> at 50,000 h<sup>-1</sup> GHSV. 2 h test duration at each condition.

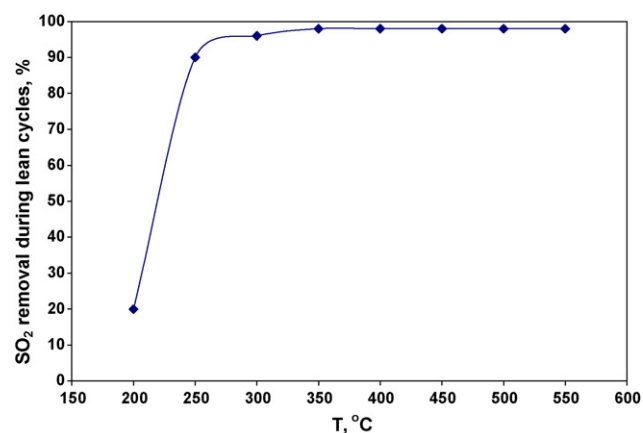
observed. However, it was a surprise to us that no Pt doping effect was observed. It indicates that Pt doping in the absorbents is not necessary. Pt had been added as a catalyst to oxidize SO<sub>2</sub> to SO<sub>3</sub> for better sulfur absorption.

To verify that Pt doping is not necessary, an absorbent with no Pt (5 wt% Ag-SiO<sub>2</sub>, sample 120C) was prepared and its performance was evaluated from 200 to 550 °C, cycling with 40 s rich feed at 10,000 h<sup>-1</sup> GHSV and 4 min lean feed with 5.15 ppm SO<sub>2</sub> at 100,000 h<sup>-1</sup> GHSV. Fig. 11 gives its SO<sub>2</sub> removal efficiency during lean cycles at different temperatures. The total duration of the cycling test with sample 120C was 16 h (206 lean/rich cycles). Without any Pt, the absorbent still gave good SO<sub>2</sub> removal performance. The role of Pt (oxidizing SO<sub>2</sub> to SO<sub>3</sub> for the formation of Ag<sub>2</sub>SO<sub>4</sub>) appears to be adequately handled by the Ag component. An absorbent without any Pt doping would have economic benefits over the Pt-containing ones.

Absorbents using other materials for the Ag support, such as Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and TiO<sub>2</sub>, were also synthesized and tested. Under lean conditions, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> reacted with SO<sub>2</sub> at temperatures >450 °C, and these sulfates could not be regenerated during the subsequent rich cycles. This caused unstable and deteriorating performance of the absorbents, perhaps by loss of surface area of the support and sintering of the Ag phase. TiO<sub>2</sub> did not react with SO<sub>2</sub> under lean conditions, making it similar to SiO<sub>2</sub> in this regard. However, large amounts of COS were produced during the rich cycles, which is undesirable. Also, the low temperature performance of



**Fig. 10.** Pt loading effect on the performance of *x* wt% Pt-5 wt% Ag-SiO<sub>2</sub> absorbents. Cycling with 20 s rich feed at 20,000 h<sup>-1</sup> GHSV and 4 min lean feed with 25 ppm SO<sub>2</sub> at 50,000 h<sup>-1</sup> GHSV. 2 h test duration at each condition.



**Fig. 11.** SO<sub>2</sub> removal efficiency of sample 120C (5 wt% Ag-SiO<sub>2</sub>) during lean cycles at different temperatures. Test condition: cycling with 40 s rich feed at 10,000 h<sup>-1</sup> GHSV and 4 min lean feed with 5.15 ppm SO<sub>2</sub> at 100,000 h<sup>-1</sup> GHSV.

the TiO<sub>2</sub>-supported absorbents was not as good as those employing fumed SiO<sub>2</sub>. Different SiO<sub>2</sub> sources, including silica gels and mesoporous silica MCM41, were also tested as supporting materials for the absorbent. We found that the large pore volume in these SiO<sub>2</sub> sources prevented the fast egress of SO<sub>2</sub> from the absorbent during rich cycles. As a result, the regenerability of the absorbents using these SiO<sub>2</sub> sources as support was not good. Therefore, due to its high stability, relatively high surface area and low pore volume, Cab-O-Sil® fumed silica was found to be the best support for Ag-based fast regenerable SO<sub>2</sub> absorbents.

#### 4. Conclusions

The thermal instability of Ag<sub>2</sub>O (relative to Ag metal) under fuel-lean conditions at 230 °C and above makes it possible to develop a Ag-based fast regenerable SO<sub>2</sub> absorbent. This absorbent can operate under the lean-rich cycling conditions proposed for NO<sub>x</sub> traps. Ag particles can effectively oxidize SO<sub>2</sub> to SO<sub>3</sub>, facilitating the formation of Ag<sub>2</sub>SO<sub>4</sub> and requiring no additional oxidation catalysts. Over a temperature range of 300–550 °C, a Ag-based absorbent with an composition of 5 wt% Ag-SiO<sub>2</sub> absorbs almost all of the SO<sub>2</sub> in the simulated exhaust gases during the lean cycles and can be fully regenerated during the following short rich cycles at the same temperature. The chemically inert fumed SiO<sub>2</sub> support provides good long-term stability. This absorbent shows great potential to protect the particulate filter and the NO<sub>x</sub> trap in the lean-burn engine after-treatment system from sulfur poisoning.

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